

EXPERIMENTAL ACID WEATHERING OF Fe-BEARING MARS ANALOG MINERALS AND ROCKS: IMPLICATIONS FOR AQUEOUS ORIGIN OF HEMATITE-BEARING SEDIMENTS IN MERIDIANI

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Introduction: A working hypothesis for Meridiani evaporite formation involves the evaporation of fluids derived from acid weathering of Martian basalts and subsequent diagenesis [1, 2]. However, there are no reported experimental studies for the formation of jarosite and gray hematite (spherules), which are characteristic of Meridiani rocks from Mars analog precursor minerals. A terrestrial analog for hematite spherule formation from basaltic rocks under acidic hydrothermal conditions has been reported [3], and we have previously shown that the hematite spherules and jarosite can be synthetically produced in the laboratory using Fe³⁺-bearing sulfate brines under hydrothermal conditions [4]. Here we expand and extend these studies by reacting Mars analog minerals with sulfuric acid to form Meridiani-like rock-mineral compositions. The objective of this study is to provide environmental constraints on past aqueous weathering of basaltic materials on Mars.

Experimental: San Carlos forsterite (SCF), siderite from Londonderry, Nova Scotia, Canada (SL) containing inclusions of ankerite, and an olvine-rich basalt from Kona, Hawaii (OB) containing plagioclase and pyroxene phenocrysts (here after collectively called samples) were ground in acetone to <75 µm and air-dried. SCO and OB had low iron contents compared to SL (Table 1).

Table 1. Major element concentration in the samples used for the hydrothermal reactions.			
	Olivine (SCO)	Siderite (SL)	Basalt (OB)
Oxide	Wt%		
SiO ₂	40.26	0.50	45.77
Al ₂ O ₃	0.25	0.15	13.05
Fe ₂ O ₃ T	10.42	74.03	10.94
MgO	47.83	21.87	15.63
CaO	0.24	1.65	12.28
Na ₂ O	0.10	0.08	1.23
K ₂ O	0.01	0.03	0.02
Total	99.57	99.93	100.11

Experimental alteration conditions for each mineral/rock consisted of six acid treatments with increasing rock/fluid (R/F) ratios. For example, SCO treatments consisted of 0.1, 0.25, 0.5, 1.00, 2.50, and 5.00 g each of SCO plus 0.2 g of sodium perchlorate monohydrate mixed with 10 ml of 0.5 M sulfuric acid (R/F ratio of 0.01, 0.025, 0.05, 0.1, 0.25, and 0.5, respectively). The reactants were placed in hydrothermal vessels and heated at 150°C for 22.5 h. At the end of each experimental run, vessels were cooled to 25°C, the solution pH recorded, and the solid residues were washed with deionized water and freeze-dried. Each supernatant was freeze-dried separately to recover evaporite forming salts. Quantitative mineralogy of the products was determined by X-Ray diffraction analysis followed by

Rietveld refinement. Morphological and chemical characterization was performed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The same experimental procedure was repeated for SL and OB. In high R/F treatments of SCO and OB, the products were harvested in two layers - a bottom layer with unreacted olivine, and a top layer where gelatinous silica and hematite were found.

Results: The products for all samples were related to the the composition of the samples and the R/F ratio (see Table 2).

Acid buffering: The six hydrothermal treatments represent varying R/F environmental weathering conditions. The addition of samples caused a rise in pH from a measured value of about 0.47 for 0.5M H₂SO₄ to a final value between 3 and 5 at the end of the reaction depending on the sample (Fig. 2). Rising pH indicates acid consumption and neutralization. Judging from the final pH values for the R/F = 0.5, the acid neutralizing ability of the samples on a weight basis are in the order: SL > SCO > OB.

Hematite formation: For all three experiments, the hematite formation peaks (highest quantity) around a R/F of 0.025-0.05 (Fig. 2a-c). The peak hematite content is commensurate with the iron content of the samples, i.e., SL with the highest iron content produced the most hematite and SCO and OB had less hematite (Table 1 & Fig 2a-c). The hematite that formed in the peak region in all three cases was gray in color with a spherical morphology (e.g., Fig. 2d,f). The low R/F treatment (i.e., 0.01) was too acidic for Fe(III)-hydrolysis. At intermediate R/F (0.05-0.1) both Fe²⁺ oxidation and ferric hydrolysis occur to form hematite and/or jarosite. At high R/F ratio treatments (i.e., 0.5) the insoluble products consisted of hematite spherules with some red hematite, sulfate minerals and unreacted sample (Table 2).

Sulfates and Evaporitic salts: No jarosite was detected for SCO reactions; however, SL and OB produced jarosite in 0.025 and 0.05 R/F experiments, respectively (Fig. 2b,c). Hematite spherule formation began when the pH was around 1 and jarosite and alunite appear at a slightly lower pH. The formation of jarosite is consistent with its stability at low pH where as in the high R/F treatments, jarosite may have precipitated initially in the high R/F treatments, but hydrolyzed to hematite as the pH increased (pH~1-3). In the OB, alunite precipitated along with jarosite, but at a much higher concentration than jarosite (Fig. 2c). Alunite precipitation is expected because OB contains considerable Al (Table 1). The alunite content was high even at high R/F treatments (Fig 2c) compared to jarosite which formed only at much lower R/F and hence much lower pH.

Evaporation (freeze-drying) of supernatants resulted in the formation of Mg-sulfate (kieserite, pentahydrate and hexahydrate) and perchlorates.

Implications for Meridiani Planum: Acidity in our experiments was caused by H₂SO₄ and by ferric hydrolysis

after oxidation of the Fe^{2+} . However, Meridiani rocks may have undergone dissolution and oxidation in two different steps; first acidic ground water with dissolved Fe^{2+} formed elsewhere and in a second step transported to the Meridiani aeolian sediments where it was oxidized and hydrolyzed to form jarosite, hematite and other sulfate-rich sediments [5].

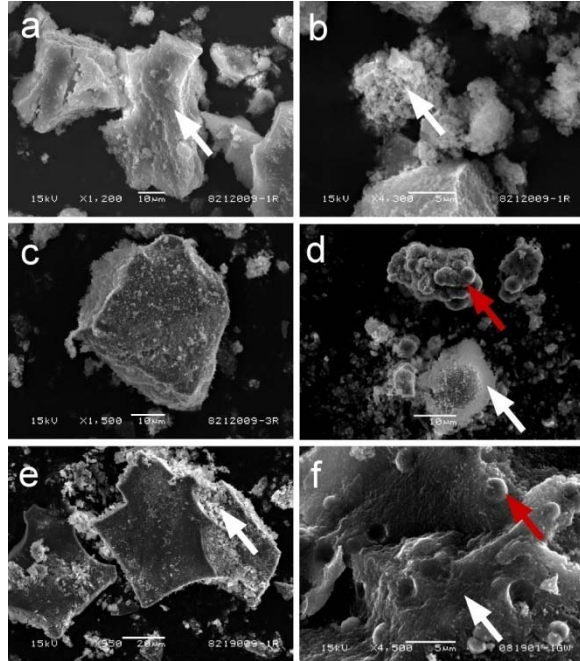


Figure 1: Scanning electron microscopy (SEM) images of selected treatments of H_2SO_4 -San Carlos olivine reaction: (a) Products for lowest rock/fluid ratio ($\text{R/F} = 0.01$) indicating amorphous silica pseudomorphs of olivine fragments (white arrows); (b) same as above showing dispersed amorphous silica indicating breakdown of the silicate network (white arrow); (c) $\text{R/F} = 0.05$ indicating a surface rind of amorphous silica; (d) same as above showing gelatinous layer material containing hematite spherules (red arrow) and amorphous silica (white arrow); (e,f) $\text{R/F} = 0.10$ showing partially reacted olivine (arrow) (e) and silica pseudomorphs of olivine fragments (white arrow) with embedded hematite spherules (red arrow) (f).

An alternate hypothesis is that oxidation and ferric hydrolysis occurred *in situ* with the aid of an oxidant akin to the the experiments in this study.

Conclusions: The hematite spherules in Meridiani outcrop may provide key clues on how the sediments formed. There are several proposed mechanisms for their formation including deposition from standing bodies of water [6], precipitation under hydrothermal conditions [4,7,8], concretion formation from stagnant ground water [5] and others (see [7]). We show for the first time that spherical, gray hematite (although smaller than Meridiani spherules) along with jarosite can be produced in the laboratory from natural Mars analog materials. Two key requirements for their formation are hydrothermal conditions and R/F ratios of 0.025-0.05 or water/rock ratios of 40 to 20. We propose that jarosite in Meridiani sediments formed in water-rich sediments enhanced by hydrothermal conditions, further hydrolysis and evaporation of these fluids resulting in precipitation of hematite and evaporite salts. Our experiments also suggest that alunite may have

precipitated along with jarosite in Meridiani sediments. Additional experiments are underway to produce larger, more Meridiani-like hematite spherules under stationary and flow-through conditions.

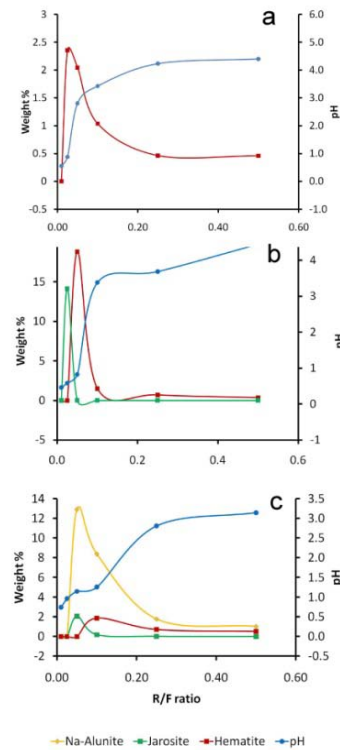


Figure 2. Hematite, jarosite and alunite abundance (wt%) of total water insoluble products for different R/F ratios for (a) SCO, (b) SL (c) OB. pH is on the second right axis.

Table 2. Water insoluble phases in olivine, siderite and basalt treated at different R/F ratios. (as = amorphous silica, hem = hematite, gtr = goethite trace, jrs = Na-jarosite, alu = Na-alunite, an = anorthite, px = pyroxene, anh = anhydrite, ank = ankerite, sd = Mg-siderite)						
R/F	0.01	0.025	0.05	0.1	0.25	0.5
Olivine (SCO)	as	as hem	as hem fo	as hem gtr fo	as hem fo	as hem fo gtr
Siderite (SL)	none	jar	hem	hem anh ank	hem anh sd	hem anh sd
Basalt (OB)	as an	as an px anh	as alu jrs an px anh	as alu jrs an px hem	as hem jrs an px fo alu	as hem an px fo alu jrs

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References: [1] Bannin et al., (1997) *JGR*, **102**, 13,341– 13,356. [2] Tosca, N. J., et al., (2005), *EPSL*, **240**, 122-148. [3] Morris et al., (2005) *EPSL*, **240**, 168-178. [4] Golden et al., (2008), *American Mineral.*, **93**, 1201-1214. [5] McLennan et al. (2004) *Science*, **306**, 1709-1714. [7] Fan et al. (2010) *Planetary and Space Science*, **58**, 401-410. [8] Catling and Moore (2003) *Icarus*, **165**, 277-300.